# Suitability of coal fly ash for the development of geopolymer binders: effects of precursor properties and synthesis parameters

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## Abstract

Coal fly ash (FA) is of high interest as a precursor material for the synthesis of geopolimer binder, representing a waste stream which is readily available from existing industry [1]. FA is not a "standard product" as its physical and chemical properties vary not only from source to source but also over time from the same power station [2]. UK Department of Energy and Climate Change listed 14 coal fuelled power stations operational in 2014, representing 26% of total generated [3]. FA production in UK is estimated at about 6·106 t per annum, half of which is sent to landfill, whereas about 114·106 t of FA is available in stockpiles [4], confirming a significant potential availability for FA-based geopolymer concrete production. The suitability of such available ashes has not been thoroughly investigated yet.

This paper analyses the factors affecting the reactivity of FA for the synthesis of geopolymer concrete, investigating physical and chemical properties of precursor materials, activator dosages and curing conditions. Detailed characterisation was carried out on thirteen FA sources from the UK. The most important factors affecting the reactivity were found to be the particle size, the loss on ignition (LOI) and the amorphous content of precursor FA. Alkali-activated FA required heat curing and medium to high alkali dosages. Strengths exceeding 70 MPa at 28 days were obtained. Microstructural characterisation with SEM coupled with EDX performed on FA pastes allowed to identify N-A-S-H gel as main reaction product.

## 1. Introduction

Alkali Activated Binders (AABs) have been studied for the last 40 years [2] and have applications in ceramics, hazardous waste containment, fire-resistant construction materials and refractories [5, 6]. One of the most interesting applications is their use as a cement-free binder that can replace Portland cement-based pastes in construction materials such as concrete and mortar products, not only for the environmental benefits arising from the avoidance of $CO_2$ emissions associated with PC production, but also in terms of their performance and durability, where such properties are not only equivalent, but often better than those achieved with PC.

The nature of the reactions occurring for the creation of an amorphous gel from fly ash are complex and still not fully understood, but in general three processes that take place contemporaneously have been identified [7]: *Dissolution of the aluminosilicate solids:* aluminosilicates from the precursor material are dissolved by alkaline hydrolysis in the high pH solution of the concentrated alkaline activator, forming a solution of silicate, aluminate and aluminosilicate species; *Gel Formation:* species released by dissolution are held in the aqueous phase, which may also contain silicate present from the activating solution. This supersaturated aluminosilicate solution forms a gel as oligomers form long chains and networks, releasing complexing water, which resides in pores; *Polycondensation:* the gel species continue to rearrange and reorganize, forming an increasingly larger network. This results in the three-dimensional aluminosilicate network of the geopolymer binder.

The dense inorganic polymer that forms the geopolymer binder provides physicochemical features that may be superior to Portland cement systems. The interconnected framework that gives geopolymers high compressive strengths [7, 8], whereas, due to the microstructure of the reaction products, geopolymer and AAB can show good to very good resistance to chemical degradation (sulphate attack, acid attack, seawater attack) [2]. Geopolymer matrix shows high thermal and fire resistance up to 1000-1200 °C [8], and geopolymers may exhibit rapid setting without long term deterioration of strength [7].

Of particular interest is the selection of precursor aluminosilicate materials that arise from waste-streams or as by-product pozzolans, which are readily available from existing industries [1], such as fly ash (FA). A wide variability in chemical dosages can be found in the scientific literature related to the activation of FA systems [9], indicating that optimum proportions of alkali species (hydroxides and silicates) in the activating solution, as well as quantity of alkali per binder mass, still need to be investigated to improve our understanding of the reaction mechanisms. Curing parameters such as curing temperature and stand time, i.e. the time elapsed before the start of high temperature curing, play an important role in the full development of the reaction products.

Fly ashes are not a "standard product" as their physical and chemical properties vary considerably not only from source to source but also over time from the same power station [2]. The Department of Energy and Climate Change in its digest of UK energy statistics [3] quoted 14 power stations operational at the end of May 2014 that were using coal or coal mixed (gas/oil) fuel, representing 26% of total electricity generated. Heath et al. [4] reported that FA production in UK is estimated at about $6 \cdot 10^6$ t per annum, half of which is sent to landfill, whereas about $114 \cdot 10^6$ t of FA is available in stockpiles. The potential availability for FA-based geopolymer concrete production is therefore significant in the UK, although the suitability of such available ashes has never been investigated in a comprehensive manner.

The work described here aimed to study the effect of curing procedure and activator dosages on the strength development of FA-based mortar, and the influence of physical and chemical properties of 13 FA sources obtained from 8 UK power stations.

## 2. Materials and Methods

The chemical composition of 13 FA sources from the UK were assessed by X-ray fluorescence (XRF). Main components (detected as oxides) were on average $SiO_2$ (50%), $Al_2O_3$ (24%), $Fe_2O_3$ (8%), plus CaO (3%), $K_2O$ (2.5%) and MgO (1.7%). Other oxides were found in percentages less than 1%. Loss on Ignition (LOI) was determined on powders previously dried overnight at 105°C. Samples were ignited for 90 minutes @ 950°C in air ventilated electric muffle furnace and the mass loss was then calculated. A high variability of LOI was found among samples. Mineralogical characterisation was carried out by X-ray diffraction (XRD) using a PANalytical X'Pert PRO X-ray diffractometer. The incident X-rays were from a Copper Kα X-ray source, running at 40 kV and 40 mA. Quartz ($SiO_2$) and mullite ($3Al_2O_3 \cdot 2SiO_2$) were the main crystalline components identified. The amorphous content (identified by a broad hump in the background of the XRD pattern centred at 20 – 30° 2θ) was quantified by adding an internal standard (corundum) and performing a Rietveld method-based analysis. Laser diffraction grain size distribution was used to assess the particle size distribution of all the investigated sources of FA. The 13 FA samples were divided in three classes according to their $D_{50}$ value: low ($D_{50} < 25\mu m$), medium ($26 < D_{50} < 30.5\mu m$), and high ($D_{50} > 30.5\mu m$). FA A was the only one used to study the effect of curing procedure and activator dosages. Table 1 summarises the main results from the above mentioned characterisation tests. All FA samples conformed to the requirements of the BS EN-450 standard [10] with regards to the $SiO_2+Al_2O_3+Fe_2O_3$ (SAF), $SO_3$, CaO, MgO, and $P_2O_5$ contents, whereas three FA sources (C, H, K) had LOI higher than the maximum prescribed value (Category C).

| | A | B | C | D | E | F | G | H | I | J | K | L | M |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $D_{50}$ (μm)[1] | 23.8 | 29.2 | 41.6 | 27.3 | 20.2 | 26.5 | 30.5 | 37.3 | 32.9 | 17.3 | 34.7 | 13.2 | 91.2 |
| Amorphous (%)[2] | 82 | 89 | 86 | 90 | 79 | 76 | 75 | 83 | 86 | 87 | 75 | 79 | 81 |
| Re.$SiO_2$ (%)[3] | 42.1 | 42.9 | 37.0 | 43.6 | 38.3 | 40.3 | 38.5 | 36.7 | 43.8 | 44.5 | 34.9 | 39.7 | 41.4 |
| Re$Al_2O_3$ (%)[4] | 15.0 | 18.5 | 15.5 | 19.1 | 14.1 | 14.2 | 12.6 | 14.3 | 17.7 | 18.6 | 9.8 | 16.4 | 15.9 |
| Tot react. (%)[5] | 57.1 | 61.4 | 52.5 | 62.7 | 52.3 | 54.5 | 51.2 | 51.0 | 61.5 | 63.1 | 44.6 | 56.0 | 57.3 |
| SAF (%)[6] | 82.2 | 84.8 | 77.1 | 83.3 | 82.8 | 85.2 | 83.4 | 73.6 | 84.0 | 84.7 | 74.2 | 84.4 | 84.8 |
| LOI (%)[7] | 4.9 | 3.6 | 11.2 | 5.0 | 4.1 | 4.6 | 7.0 | 17.4 | 4.6 | 4.5 | 17.3 | 5.2 | 4.3 |
| LOI Cat.[8] | A | A | NC | B | A | A | B | NC | A | A | NC | B | A |

key: 1: grain dimension for 50% passing. 2: amorphous content calculated via Rietveld technique.
3: reactive $SiO_2$, calculated by subtracting the crystalline $SiO_2$ from the total amount determined by XRF.
4: reactive $Al_2O_3$, calculated by subtracting the crystalline $Al_2O_3$ from the total amount determined by XRF.
5: total reactive aluminosilicate, calculated from the sum of 3 and 4.
6: $SiO_2+Al_2O_3+Fe_2O_3$ content.
7: Loss on ignition.
8: Category due to the LOI according to the BS EN 450-1:2005 + A1:2007.

Commercially available alkalis were used. Laboratory grade sodium hydroxide (NaOH) in solid form was dissolved in water at the required dosage, whereas sodium silicate was supplied as a solution with the following composition: 12.8% $Na_2O$, 25.5% $SiO_2$ and 61.7% $H_2O$. The alkali dosage (M+) was defined as the percentage mass ratio of total

sodium oxide ($Na_2O$) in the activating solution to the binder. The alkali modulus (AM) was defined as the mass ratio of sodium oxide to silica in the activating solution. M+ was from 7.5% to 15%, whereas AM was from 0.5 to ∞ for the first series of experiments. The 0.5 corresponds to an all sodium silicate solution and ∞ corresponds to an all sodium hydroxide solution. A range of dosages were used to find which values gave the maximum strength. These values were then used in subsequent experiments investigating the influence of physical and chemical properties of different FA sources.

The water/solids ratio was defined as the ratio between total mass of water (i.e. added water mass + water mass in the alkali solutions) and the total solid mass (i.e. mass of binder + mass of alkali solids). This ratio was kept constant at 0.37.Well-graded, rounded quartz sand sized 0/5 mm was used for preparation of mortars. The adopted sand/binder mass ratio was equal to 2.75. A 5 l planetary mixer was used. Binder and sand were placed in the mixer bowl and mixed for one minute. The alkali solution was then added and the material was mixed for a further 9 minutes. A flow table test was then performed according to BS EN 12350-5 [11]. Mixing was continued for a further 5 minutes, giving a total mixing time of 15 minutes. The mortar was then transferred to 50 mm cube moulds and compacted on a vibrating table for 60 seconds. Moulds were then sealed by wrapping in polyethylene film.

Curing conditions were either (a) 1 hour at 20°C followed by curing at 50°C and (b) 1 hour at 20°C followed by curing at 70°C. A 300 kN capacity compression testing machine was used for all testing with a loading rate of 0.8 kN/s.

Images for microstructural analysis were acquired with either a Philips XL30 Scanning Electron Microscope equipped with an Oxford Instruments INCA energy dispersive X-ray spectroscopy (EDS) system or a Hitachi TM300 SEM equipped with a Bruker Quantax 70 EDS systems. The EDS systems allow the collection of chemical information for spots and areas in the samples. The samples comprised broken pieces (~5.0 x 5.0 x 2.5 mm) of hardened paste mounted onto aluminium stubs using epoxy adhesive, orienting the fractured surface in a convenient position towards the SEM beam also bearing in mind the location of the EDS detector. Samples were coated with a thin gold-palladium layer to provide a conductive pathway to prevent surface electrical charging.

## 3. Results and discussion

A first investigation aimed at understanding the effect of curing temperature and the effect of activator dosages on compressive strength development was carried out using Fly Ash A. Results are shown in Figure 1. It can be seen that in all cases, with the exception of those with the lowest AM (0.5), 70°C curing temperatures give significantly increased strengths compared to those cured at 50°C for the same time. The same trend was observed irrespective of the "stand time" duration. Mixes with low alkali modulus were extremely viscous and also tended to expand upon thermal curing, forming a muffin like top. Lower curing temperature leads to mitigation of such expansion and this is reflected in the increased strengths.

The observed effect of curing temperature on the mechanical strength is well documented in the literature. Investigations on reactivity of FA under thermal curing are reported to

having been carried out for temperatures in the range 30 °C to 85 °C [12]. Another study [13] found that increasing the curing temperature from 45 °C to 65 °C resulted in a 5-fold rise of mechanical strength, whereas a 10-fold rise was observed between 65 °C and 85 °C. Reaction kinetics resulting from different curing temperature were investigated with isothermal calorimetric tests on different materials (Portland cement, activated slag and fly ash, and selected fly ash– slag blends) at 25 °C, 35 °C, and 40° C, observing the development of the polymerisation [14].

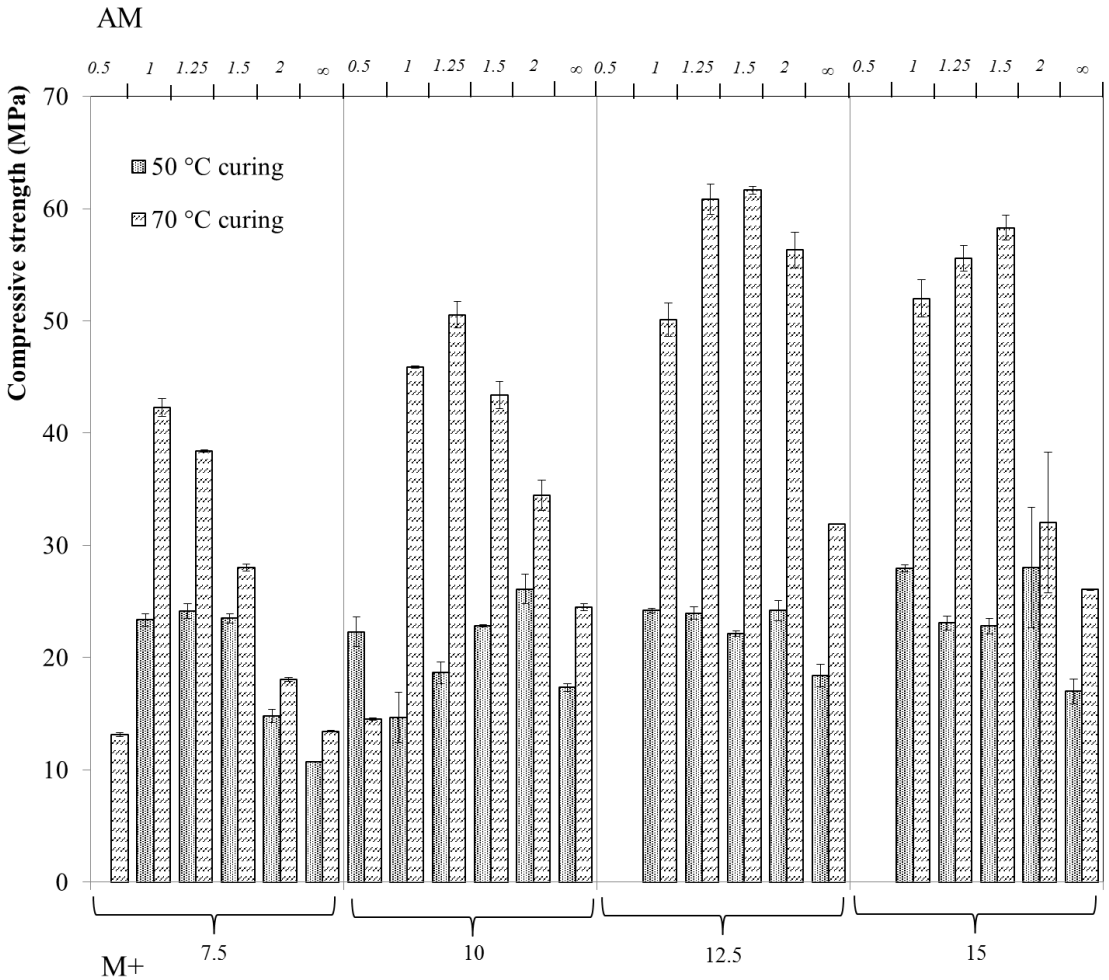


Figure 1. Compressive strengths at 28 days of 100% FA mortars for 50°C and 70°C curing temperatures for a range of alkali modulus (AM) and alkali dosage (M+).

The alkali dosage is a proxy for the alkali concentration, and describes the mass ratio of sodium oxide ($Na_2O$) in the activating solution to FA, where the water to total reactive solids ratio is fixed. An increase in alkali dosage (M+) resulted in an increase of the strength up to an M+ of 12.5%. Beyond this ‘optimum’ value, the strengths decreased, which is attributed to saturation of the gel with alkali ions resulting in less free water to be available for speciation of silica and alumina oligomers from the dissolution of FA.

The alkali modulus (AM) is the mass ratio of sodium oxide to silica in the activating solution and it is a proxy for the amount of added silica in the activator solution. An optimum range of values for the alkali modulus was identified, above and below which strengths decrease. With increasing alkali dosage, that 'sweet spot' broadens out towards higher alkali modulus. Again, results for M+ = 15% do not follow these trends. In general, alkali moduli between 1 and 1.25 give the highest strengths across the alkali dosages investigated.

The drop-off in strength with increasing modulus is likely to be due to the reduced amount of available silica that can participate in the 'reorganisation-gelation-polymerisation' steps of the geopolymer formation and thus the development of a denser and more complete and long polymer chain. The reduction in strengths at low modulus (AM=0.5: all sodium silicate) can be attributed to the reduction of the pH in the system when only sodium silicate solution is used. The expansion of the cubes upon thermal curing could also have contributed.

The optimum alkali modulus and dosage combinations resulting in a strength maximum of 70 MPa was identified at around an alkali dosage of 12.5% and alkali modulus of 1.25, cured in oven at 70 °C.

Optimum activator dosages were used for the production of geopolymer mortars with the 13 UK FA sources. Compressive strength measured at 28 days for samples cured at 70°C was plotted against physical and chemical properties, see Figure 2.

The reaction rate of FA depends on several chemical and physical factors [2, 15]. The content of Si and Al, the amorphous phase content and the loss on ignition (LOI) are important chemical factors. Particle size of the precursor materials not only affects the fresh properties (water demand, viscosity, setting time, etc.) but also affects its reactivity. The reduction of the grain size through further milling is known as mechanical activation, and it is commonly adopted for increasing the reactivity of powders. The fineness of the FA appeared therefore to correlate to the compressive strengths and to some extent with LOI, whilst no relationship was observed linking the compressive strength to amorphous content or silicon-aluminium-iron oxides (SAF) content for the investigated ashes. It may therefore be concluded that one of the most important factors to consider for achieving high compressive strengths is the grain size of the FA. It must, however, be emphasised that ten out of thirteen of the tested FA samples are suitable for use in concretes to partially replace Portland cement and thus conform to EN-450.

The basic microstructure of 100% FA paste is shown in Figure 3. The paste is made up of unreacted particles of FA in a rough and sugary looking granular gel. There are commonly gaps between the gel and the unreacted FA suggesting weak bonding of gel to unreacted particles. Some long fractures are present, but these have a morphology suggesting they formed during breakage of the sample rather than by desiccation. From EDS-based analysis it is clear that the FA cenospheres are relatively enriched in Al and depleted in Ca and Na relative to Si content. On the other hand, the rough sugary gel is relatively enriched in Na and slightly enriched in Ca relative to the unreacted FA.

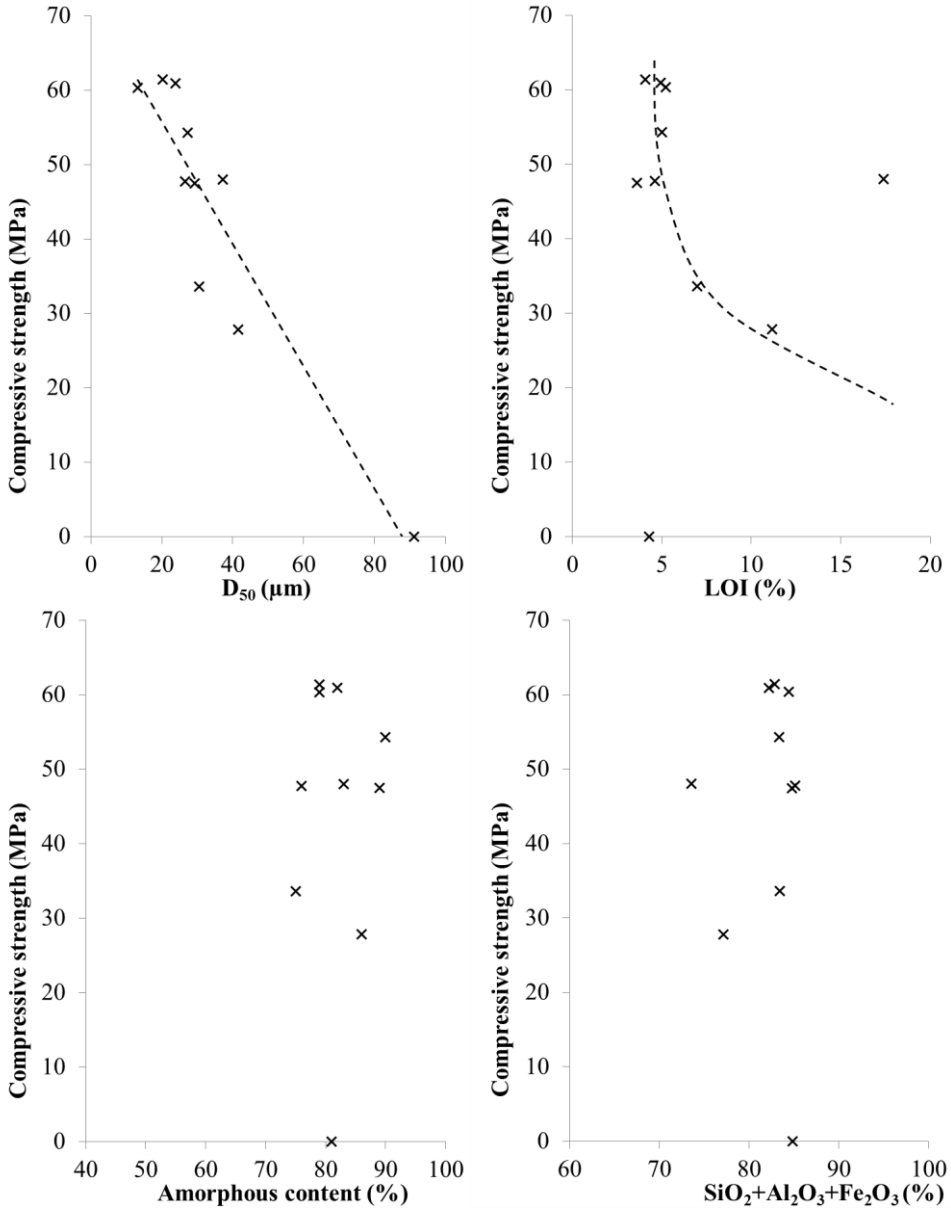


Figure 2. Mortar compressive strength vs. physical and chemical properties of 13 FAs.

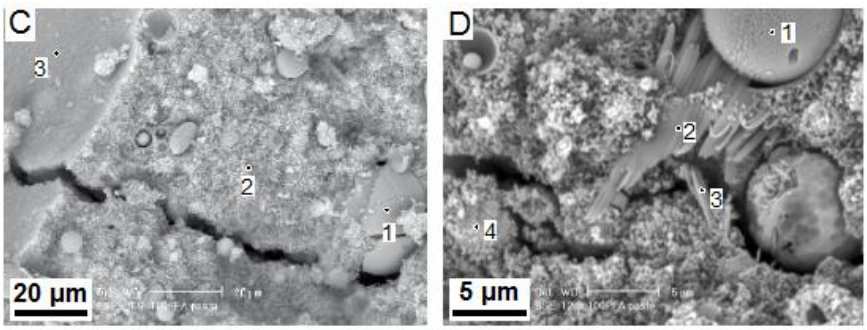


Figure 3. SEM images of 100% FA paste.

## 4. Conclusions

Geopolymer and alkali activated binders can offer a possible alternative to Portland cement concrete. The following factors affecting the mechanical properties were investigated: (a) the effect of curing procedure and activator dosages on the strength of FA-based mortar; (b) the influence of physical and chemical properties of FA sources.

Curing temperature has a very significant effect on strength of FA based geopolymers: specimens cured at 70°C were considerably stronger than specimens cured at 50°C. The dosage of activators is also very important for not only achieving the required early age properties but also for the effect on compressive strength. A 'sweet spot' of the optimum alkali modulus and dosage combinations, i.e. alkali dosage of 12.5% and alkali modulus of 1.25, gave compressive strength of ~70 MPa.

Physical and chemical properties of potential FA sources should be investigated before selecting the most suitable one. Average grain size was found to be one of the important factors affecting the potential compressive strength. Coarse FA coupled with low amorphous content and high LOI needs to be avoided. SEM investigation on pastes of 100% FA allowed to observe a sodium alumina silicate hydrate gel (N-A-S-H).

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